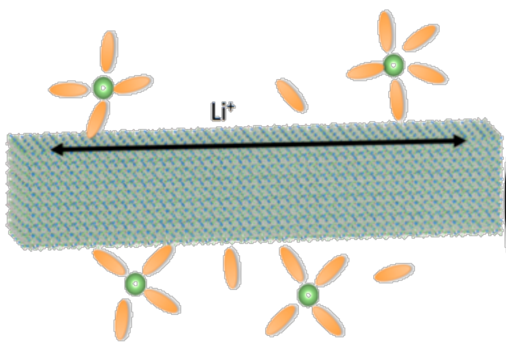
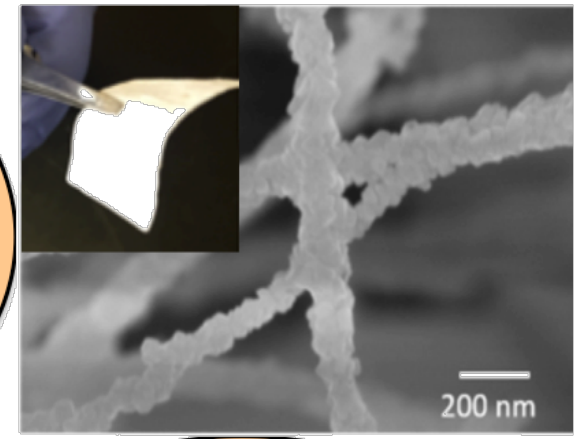
High Conductivity and Flexible Hybrid Solid State Electrolyte

Eric D. Wachsman, Liangbing Hu, Yifei Mo



MO (Computation):
- Mechanical flexibility;
- Ion transport on surface and interface;
- Li metal dendrite;
- Interface impedance.



WACHSMAN (Experiment):
- Nanofibers with optimized garnet composition, process and dimensions;
- FIB/SEM structures

Flexible, Solid State Hybrid Electrolyte

HU (Experiment):
- Hybrid electrolyte
- Li metal anode with hybrid electrolyte;
- Li-S cells with hybrid electrolyte.

Project ID: BAT322

Overview

Timeline

- Project Start: October 1, 2016
- Project End: September 30, 2019
- Percent Complete: 75%

Budget

- Total Project Funding: $1,388,889
  - DOE Share: $1,250,000
  - Cost Share: $138,889
- FY 2016 Funding received: $1,250,000

Barriers

- Solid state batteries are known for high bulk and interfacial impedance and are inherently rigid
- Organic electrolytes are less stable, flammable, have limited mechanical strength or ability to block dendrites
- A balance is needed that combines the advantages of both types of electrolytes to enable Li-metal batteries

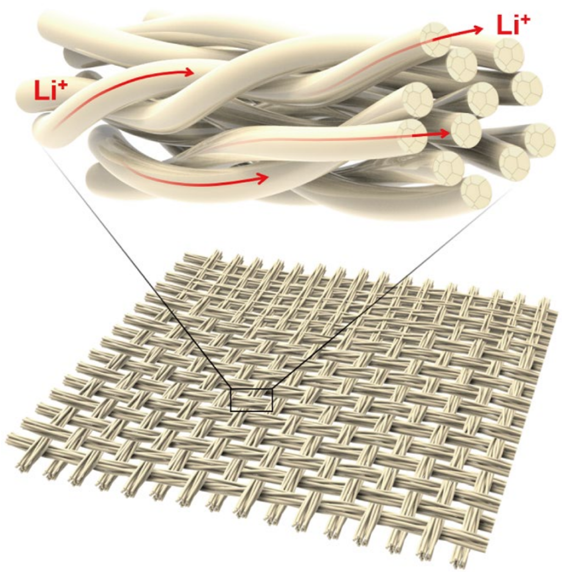
Partners

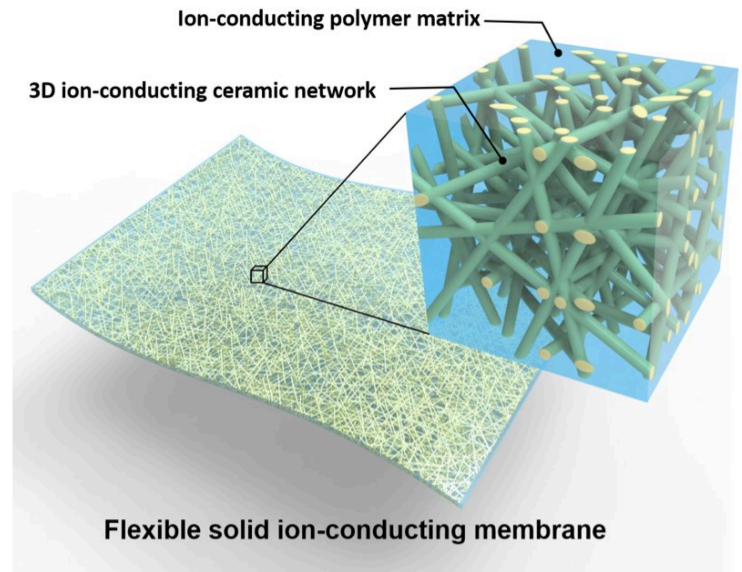
- Longstanding collaboration with Prof. Venkataraman Thangadurai

Relevance

Objectives

- Develop high-conductivity (>0.5 mS/cm), flexible, low-interfacial impedance garnet-organic hybrid electrolytes based on garnet nanofibers.
- Demonstrate Li-S batteries with ~450 Wh/kg for 500 cycles





Impact

- A hybrid flexible solid electrolyte will enable high-energy density, safe Li metal batteries with 2-3X energy density that can still be processed within existing battery manufacturing infrastructure

Milestones and Approach

Approach

Use computational modeling and experiment to:

- Determine Li diffusion, Li dendrite protection, and mechanical properties of garnet, polymer electrolytes, and hybrid electrolytes
- Characterize electrochemical, mechanical, and thermal properties of hybrid electrolytes
- Optimize hybrid electrolyte and produce full cell Li-S battery delivering 450 Wh/kg for 500 cycles

		Year 1				Year 2				Year 3			
	Name(Task, Subtask, Milestone)	Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12
1	**Task 1: Develop computational models**												
2	**Task 2: Synthesize and characterize garnet nanofibers**												
3	**Task 3: Fabricate hybrid solid state electrolyte**												
4	**Task 4: Determine structure and properties of hybrid electrolyte**												
5	**Task 5: Li-hybrid electrolyte interface**												
6	**Task 6: Fabricate and test Li-S full cells**												

FY19Q1 Milestone: Model Li dendrite protection (**Completed**)

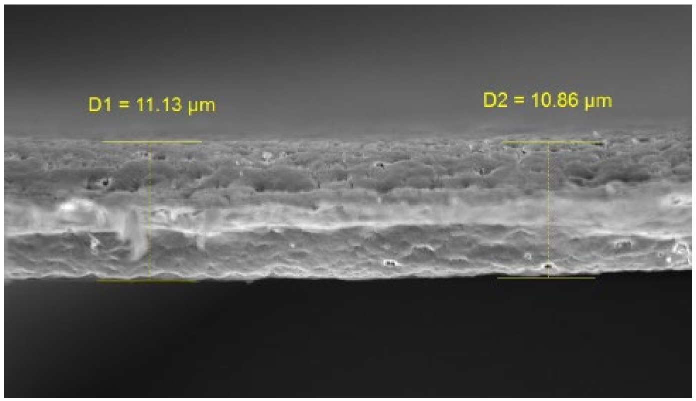
FY19Q2 Milestone: Fabricate porous mixed electron/ion conductor (**Completed**)

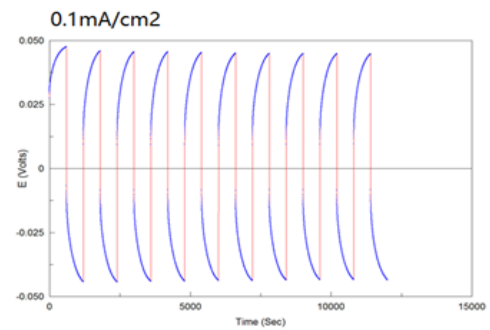
FY19Q3 Milestone: Fabricate and evaluate Li-S full cell with hybrid SSE (**In Progress**)

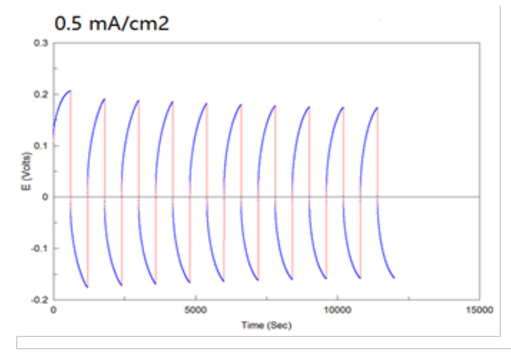
FY19Q4 Milestone: Achieve full cell performance of 450 Wh/kg **(In Progress)**

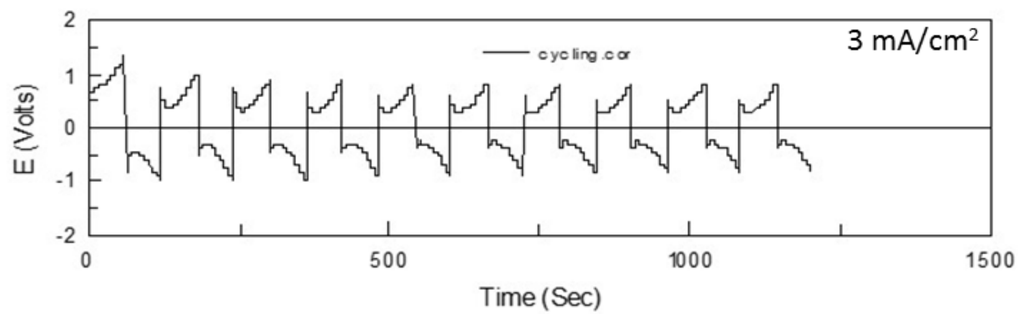
Understanding Lithium Cycling in Thin Hybrid SSE

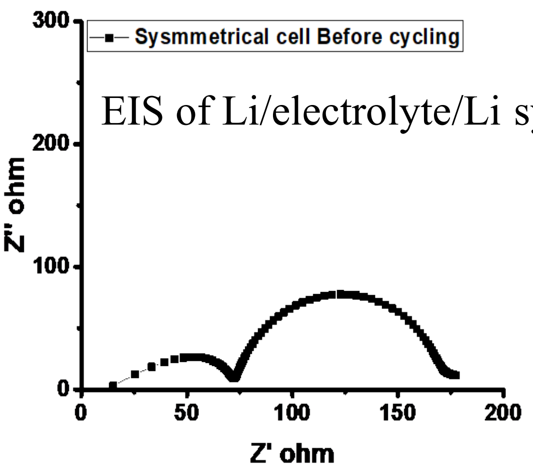
Hybrid composite electrolyte with thickness < 20 µm.









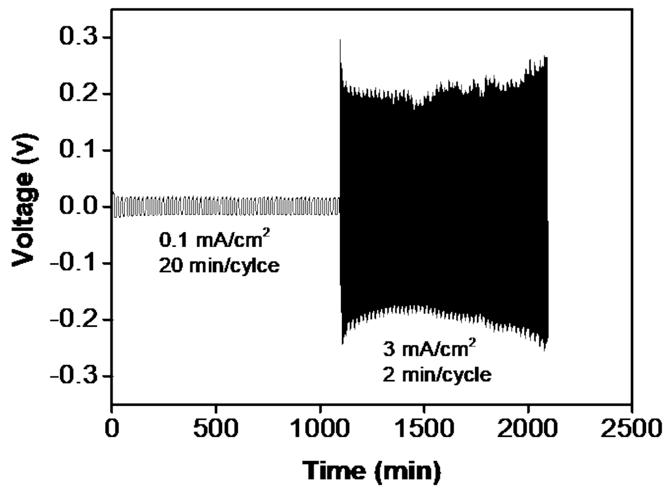


EIS of Li/electrolyte/Li symmetric cell

Initial Symmetrical cell cycled at $0.1 mA/cm^2$, $0.5 mA/cm^2$, and $3 mA/cm^2$.

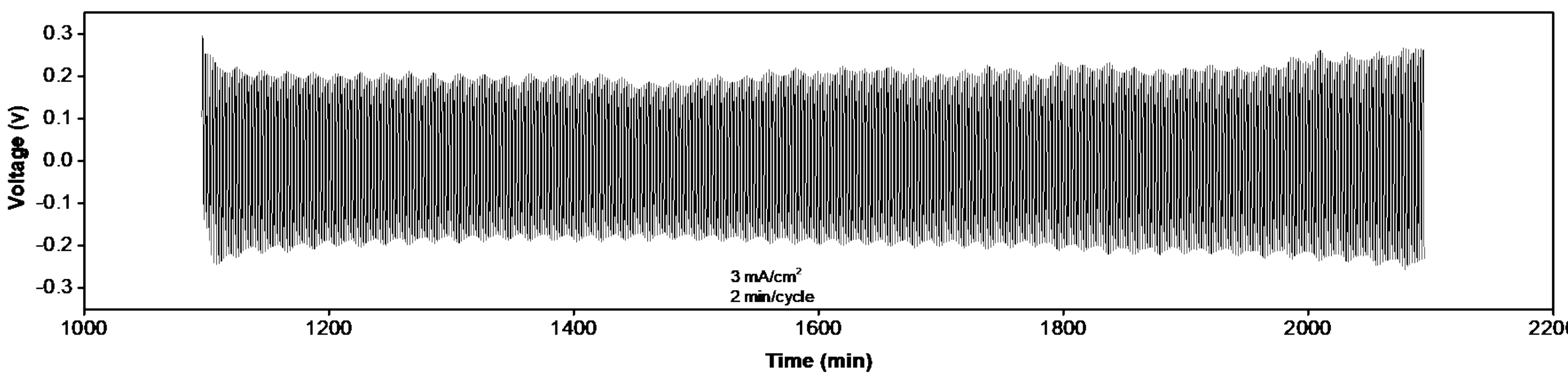
FY18Q3 Milestone: Understand Lithium stripping and plating in thin SSE at a current density of $3 mA/cm^2$ without shorting (**Completed**)

Symmetrical Cell Cycling at 3 mA/cm²



Cycling of the symmetrical cell of lithium metal/hybrid electrolyte/lithium metal assembly.

Cycling of lithium metal/hybrid electrolyte/lithium metal symmetrical cell at 3 mA/cm² for 500 cycles without lithium dendrite penetration.



FY18Q4 Milestone: No lithium dendrite for 3 mA/cm² for 500 cycles (**Completed**)

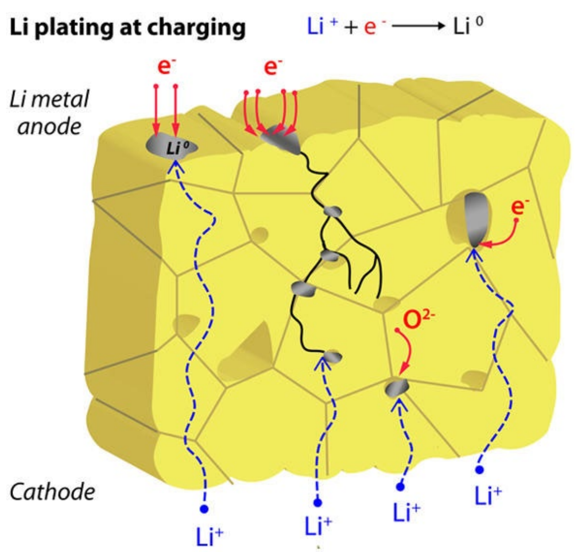
Defects and Electron Transport in Garnet and Effect on Li Formation

The formation of Li metal inside solid electrolyte involves the reduction of Li^+ into Li metal, and requires electron transport pathways. The formation of other point defects in garnet may significantly impact Li reduction and formation within garnet solid electrolyte.

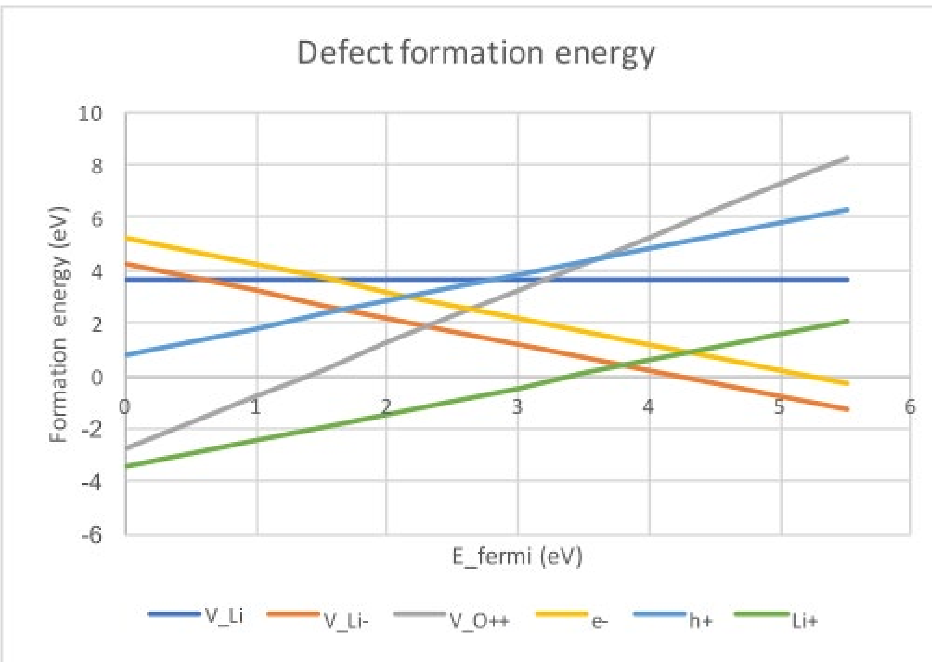
First principles calculations were performed to evaluate various point defects in garnet.

Results indicate:

- Li^+ insertion into garnet may be energetically favorable, in agreement with prior experimental studies. Ma et al. Nano letter 2016
- Oxygen vacancy V_O may form at Li rich conditions enhancing Li^+ reduction to metal.
- Electronic carriers may also form (calculated formation energy) which may enhance electron transport within solid electrolyte and dendrite formation.

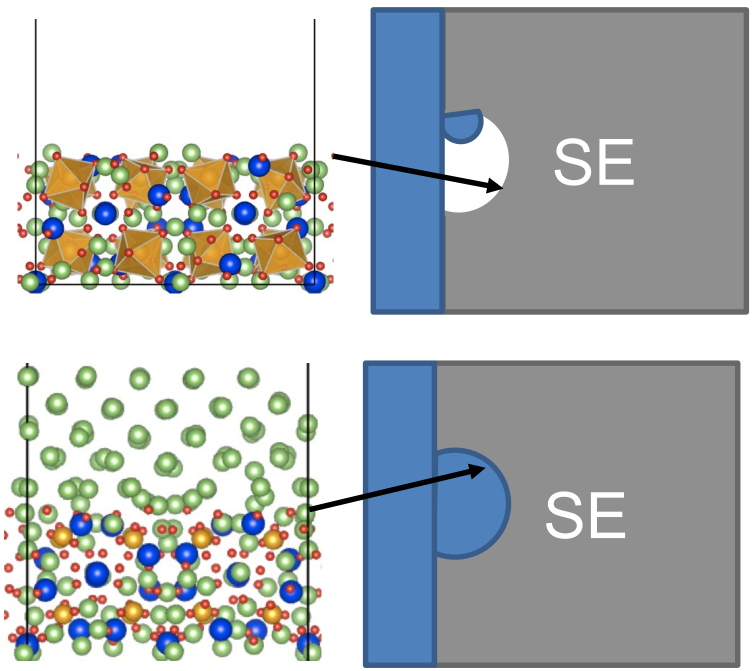


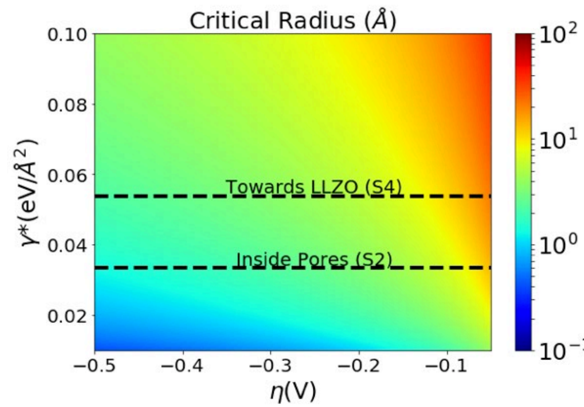
Kilner et al ACS appl mater inter 2017

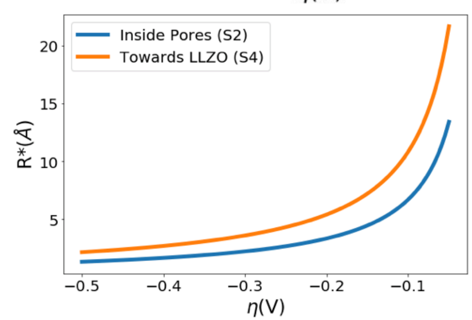


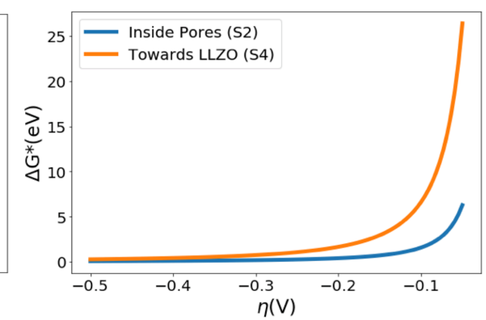
Understanding Li Formation Inside Solid Electrolyte: Li Nucleation

To understand Li dendrite growth mechanism within garnet solid electrolyte, its elementary processes steps: 1) Li metal nucleation -> 2) Li dendrite growth inside garnet solid electrolyte. Thermodynamics of Li dendrite formation is being investigated using nucleation theory based on interface energy input from the first principles calculations.







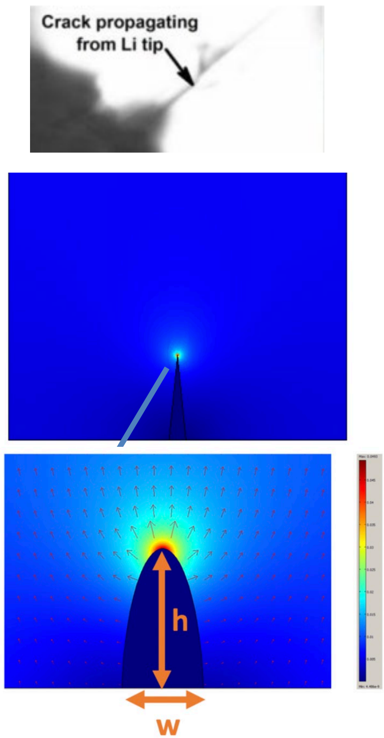


Critical nucleation barrier greatly affected by applied overpotential. At large overpotential, the critical radius is very small (~Å) suggesting easy Li metal nucleation at large overpotential. The results also found that filling of Li metal inside pores energetically more favorable than penetrating garnet.

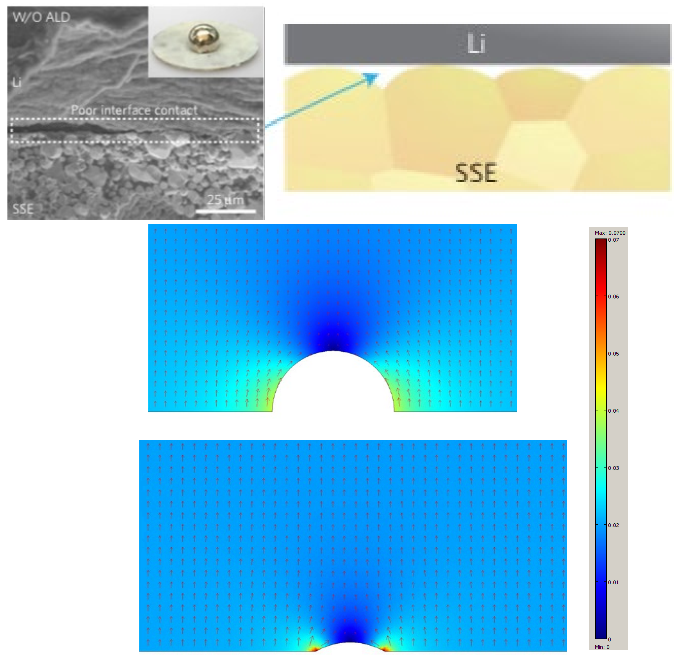
Understanding Li Formation Inside Solid Electrolyte: Li Nucleation

High overpotential and current concentration drives Li metal nucleation and formation.
Li potential and field is studied within the solid electrolyte (SSE) in variety of conditions.

Li tip in SSE

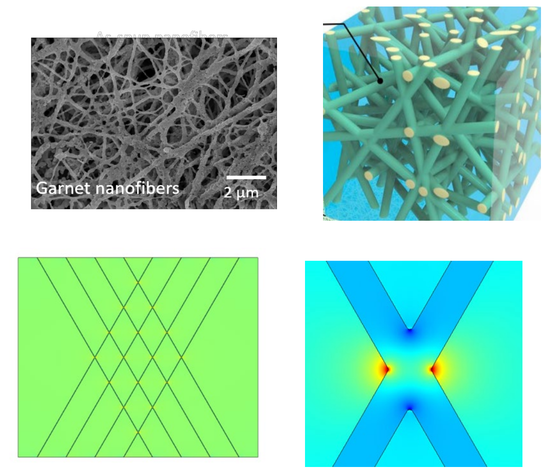


Poor Li/SSE interface contact



- Tip of Li dendrite and poor interface contact lead to highly concentrated field and current (~10-30 fold increases) resulting in strong driving force for Li metal formation.

Hybrid SSE with interconnected fast-conducting garnet fibers



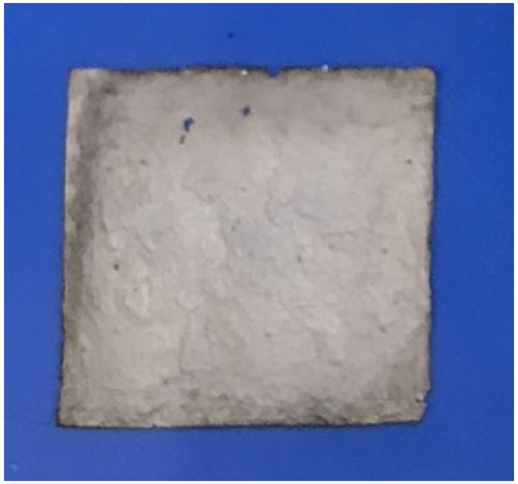
- The use of flexible composite SSE mitigates poor interfacial contact problem.
- The interconnected fast-ion conducting channels alleviates the current concentration that drives Li metal formation.

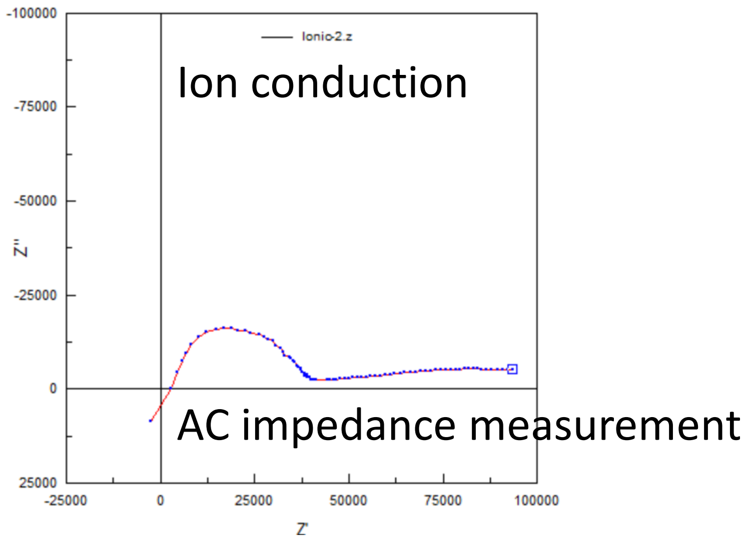
Swamy et al. JECS 2018

FY19Q1 Milestone: Model Li dendrite protection (**Completed**)

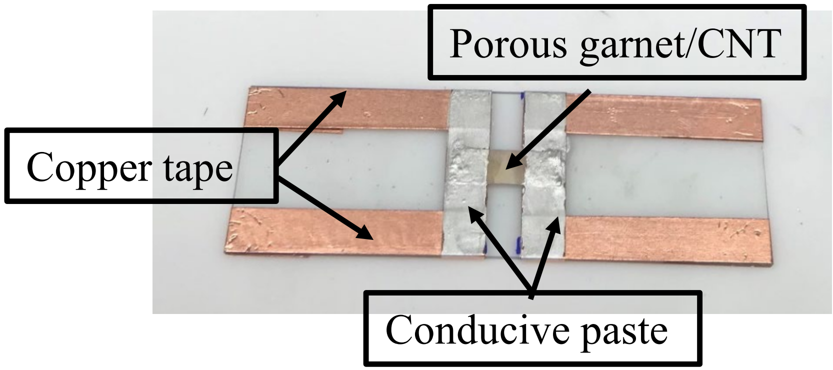
Fabricate Porous Mixed Ion/Electron Conductor

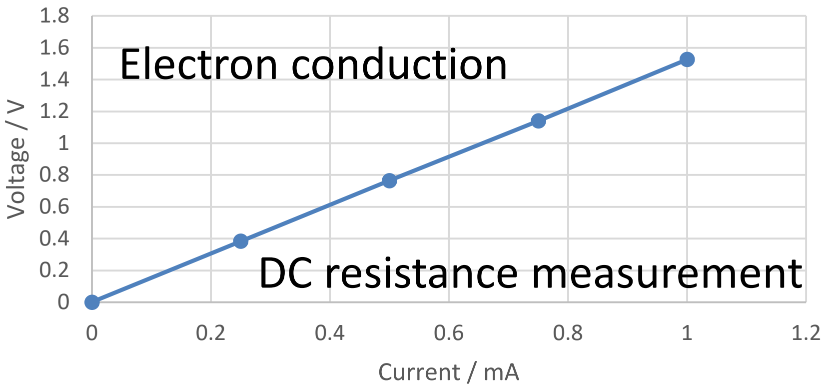
Porous garnet fiber membrane infiltrated with carbon nanotube to conduct electrons and ions





Electrochemical performance measurement

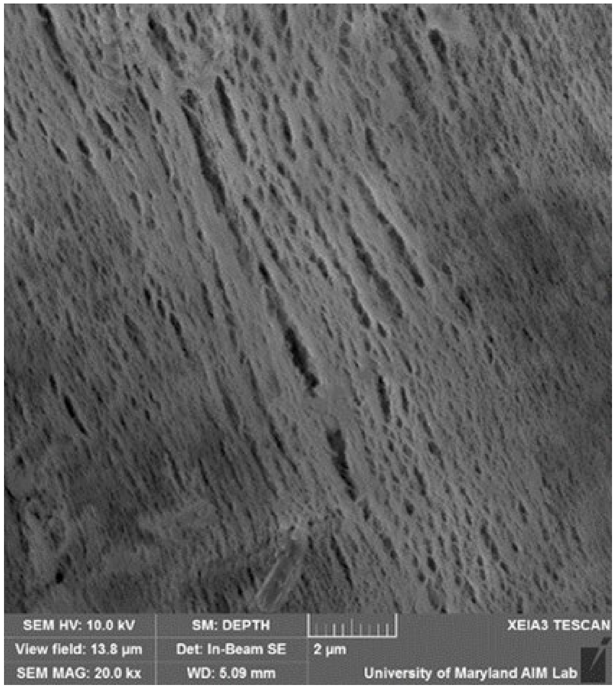




FY19Q2 Milestone: Fabricate and evaluate porous mixed electron and ion conductor (filled with S) (**Completed**)

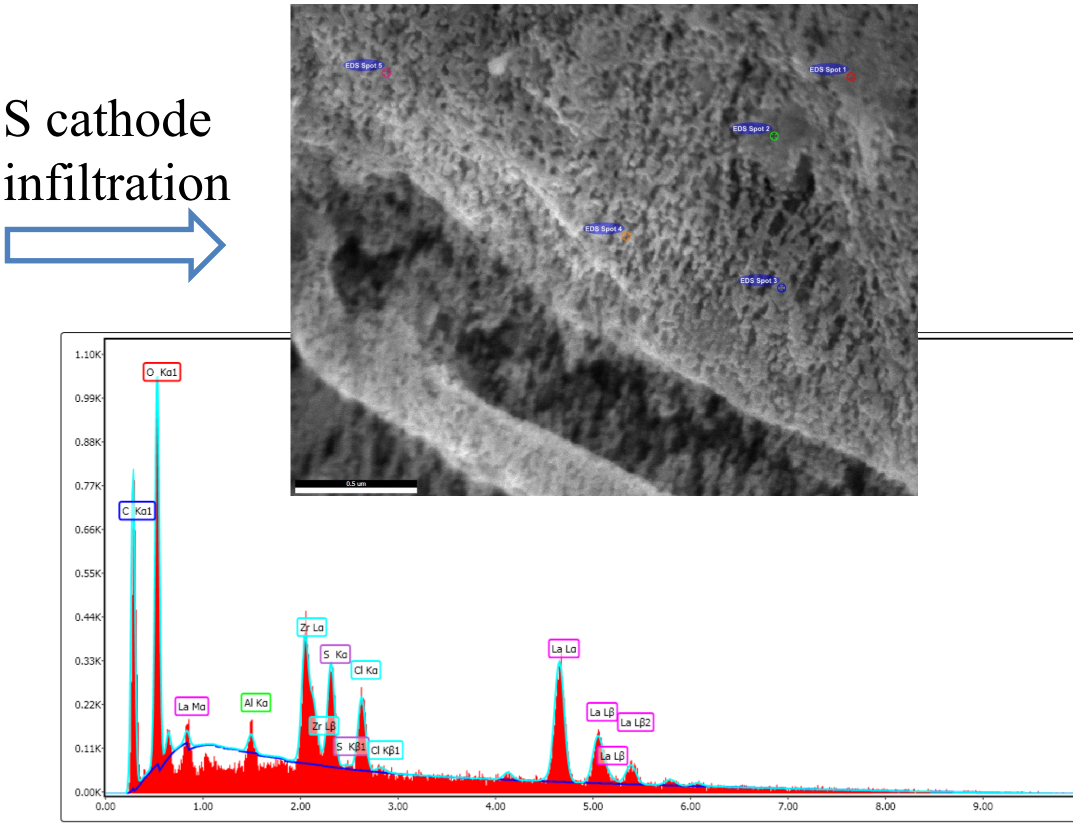
Porous Mixed Ion/Electron Conductor Infiltrated with S

As prepared garnet fiber membrane



S cathode infiltration

Carbon and S overcoated garnet fiber

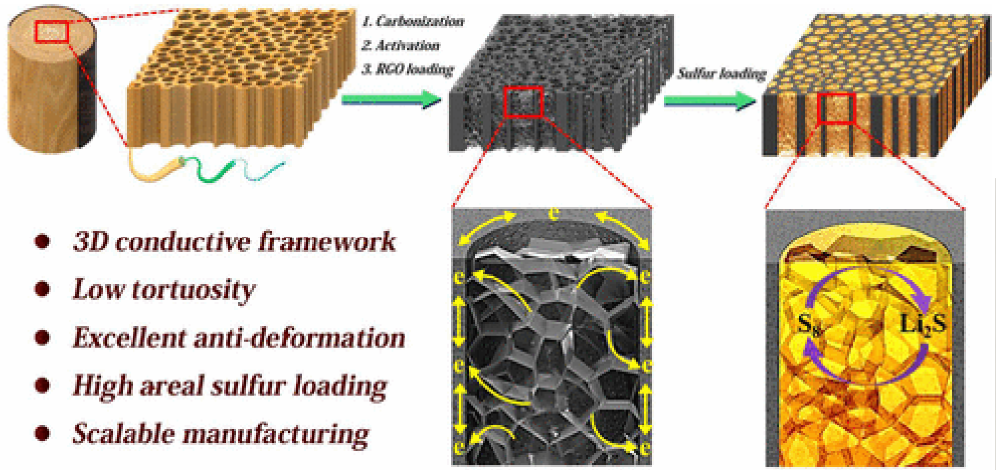


Mixed conductor filled with sulfur confirmed by elemental analysis

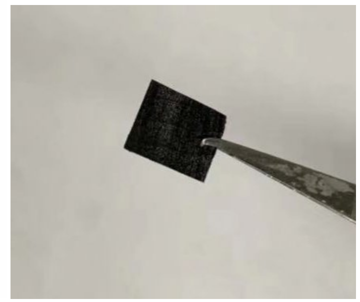
FY19Q2 Milestone: Fabricate and evaluate porous mixed electron and ion conductor (filled with S) (**Completed**)

Fabricate High-Loading S-Cathode

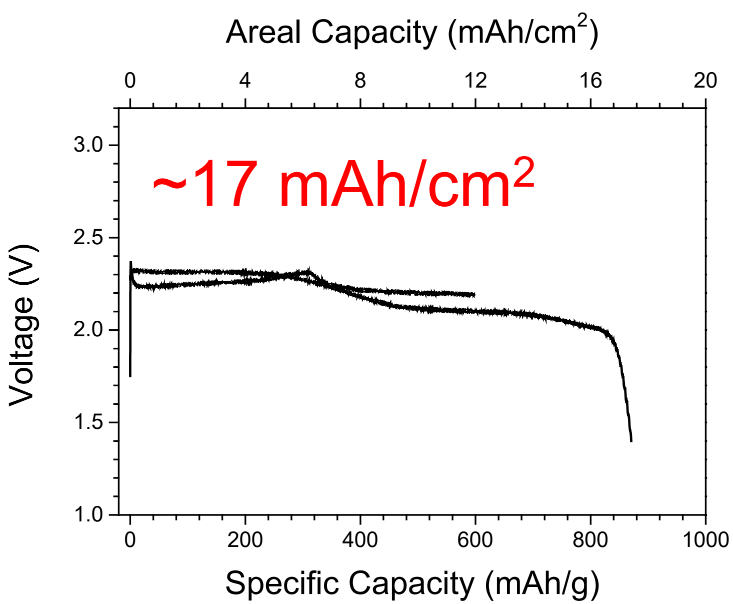
S@Graphene in Carbonized Wood with High Sulfur Loading of ~20 mg/cm²

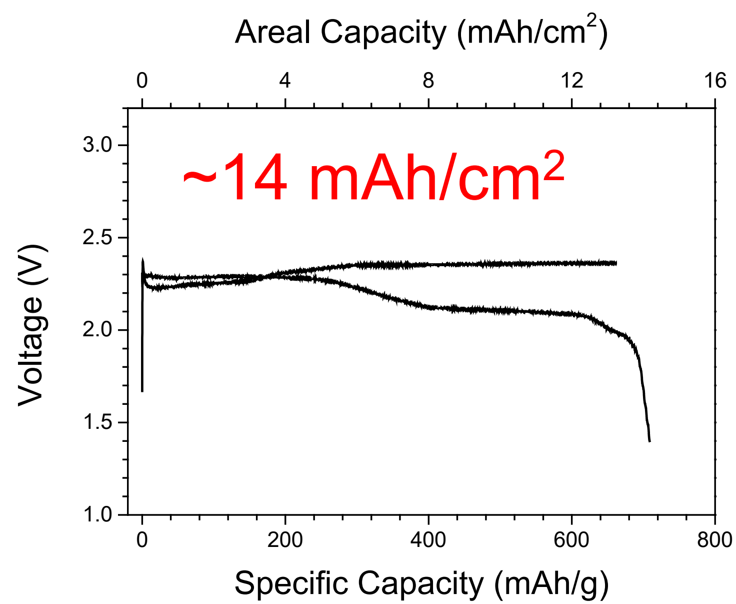


- Milestone requires 10 mAh capacity.
- To achieve this capacity 3D host materials are used for thick S cathode.



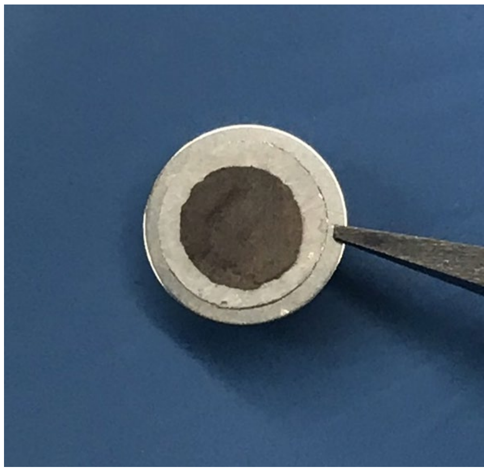
0.5 cm² cathode
20 uL electrolyte: 1 M LiTFSI – DOL/DME
Rate: 200 mA/cm²
Status: Cycling





Fabricate Li/Hybrid-SSE/S Full Cell

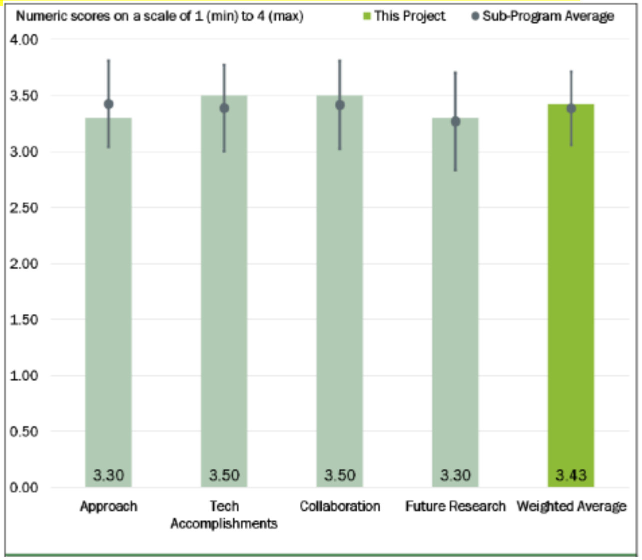
Li-SSE-S full cell assembled for testing in coin cell



Li-SSE half cell assembled for testing in pouch cell

FY19Q3 Milestone: Fabricate and evaluate of Li-SSE-S full cell with a size of 1 cm by 1 cm (**In progress**)

Response to Previous Year Comments



Comment - Approach: "team employed combined experimental/computational approach to developing solid, flexible electrolyte to enable high-performance Li-ion batteries with the goal of achieving an energy density of 450 Wh/kg. The team has developed a garnet textile-reinforced, hybrid composite-polymer electrolyte…and has made remarkable progress in addressing technical barriers."
Response: We appreciate the reviewers comments

Comment – Technical Accomplishments and Progress: "Based upon goals of project, the reviewer reported that PI has definitely achieved the targets although would not be a real-world solution due to the issues with PEO" and other comments regarding polymer selection. Suggestions for perpendicular (vs parallel) garnet fiber orientation and better integration of experiments and modeling.
Response: PEO was evaluated due to potential to minimize dendrites in hybrid SSE but we plan to use other organic electrolytes in future. Parallel orientation of garnet fibers in SSE based on need to achieve 20 μm thickness milestone but evaluating perpendicular in electrode structure. Experiment and computation are currently consistent, but goal for theory become more predictive in future.

Comment – Collaboration and Coordination: "team consists of three PIs with complementary expertise and excellent coordination among team"... but want to see team publications and suggest more external collaboration.
Response: We welcome additional collaboration and team publication list given in additional slides.

Comment – Proposed Future Research: "reviewer remarked that the future plan…is very relevant and will uncover many of the integration issues that were previously discussed; in addition, this will provide the research team a chance to produce another innovative solution.." also a suggestion to test mechanical properties.
Response: We appreciate comments, will try to test mechanical properties but focused on cell electrochemical milestone

Comment – Relevance: "reviewer found research to be relevant to the DOE efforts in developing safer, high-energy density, high-power density, solid-state batteries with metallic Li anodes, including Li-sulfur batteries that can be processed within the existing battery-manufacturing infrastructure. This project particularly addresses the development of highly conducting and mechanically stable solid-composite electrolytes."
Response: We appreciate the reviewers comments

Collaboration and Coordination

Continued collaboration among 3 co-PIs at UMD and with Prof. Venkataraman Thangadurai University of Calgary (co-inventor of garnet)

Remaining Challenges and Upcoming Work

Demonstrate high energy (450 Wh/kg) density Li-S cells with the thin hybrid electrolyte

Proposed Future Research

FY19

- Demonstrate Li-S cells with 450 Wh/kg
- Integrate computational and experimental results

Any proposed future work is subject to change based on funding levels.

Summary

FY 2017

- Developed multiple approaches to make flexible hybrid polymer/garnet fiber electrolyte membranes
- Fabricated flexible and scalable 4 cm X 4 cm garnet fiber mat
- Synthesized polymer garnet fiber hybrid electrolyte with good conductive properties

FY 2018

- Developed fundamental understanding of Li diffusion in garnet nanofibers and response to mechanical deformation
- Analyzed microstructures with FIB/SEM, AFM and profilometer
- Characterized electrochemical, mechanical and thermal properties of hybrid SSE.
- Fabricated thin hybrid SSE with a thickness of ~ 20 μm
- Achieved 3 mA/cm^2 Li cycling for 500 cycles with thin hybrid SSE and no shorting

FY 2019

- Developed fundamental understanding of Li-dendrite formation in garnet/hybrid SSE
- Developed mixed ion/electron conducting garnet/carbon electrode structures
- Achieved high Sulfur loading cathodes
- Fabricated Li/hybrid-SSE/S cells

Backup Slides

Team Publications

- "Garnet-type Solid-state Electrolytes: Materials, Interfaces, and Batteries” C. Wang, K. Fu, S. P. Kammampata, D. W. McOwen, L.i Zhang, G. T. Hitz, A. M. Nolan, A. Samson, Y. Mo, E. D. Wachsman, V. Thangadurai, L. Hu, *Chemical Reviews* (submitted)
- “Nature-Inspired Aligned Garnet Nanostructures,” J. Dai, K. Fu, Y. Gong, J. Song, C. Chen, Y. Yao, G. Pastel, E. D. Wachsman, L. Hu,. *Nano Energy* (submitted)
- “Lithium-Ion Conductive Ceramic Textile: A New Architecture for Flexible Solid-State Lithium Metal Batteries,” Y. Gong, K. Fu, S. Xu, J. Dai, T.R. Hamann, L. Zhang, G.T. Hitz, Z. Fu, Z. Ma, D. McOwen, X. Han, L. Hu, and E. D. Wachsman, *Materials Today*, **21**, 594-601 (2018).
- “Computation-Accelerated Design of Materials and Interfaces for All-Solid-State Lithium-Ion Batteries”, A. Nolan, Y. Zhu, X. He, Q. Bai, Y. Mo, *Joule*, **2**, 2016-2046 (2018).
- “Design Strategies, Practical Considerations, and New Solution Processes of Sulfide Solid Electrolytes for All-Solid-State Batteries”, K. H. Park, Q. Bai, D. H. Kim, D. Y. Oh, Y. Zhu, Y. Mo, Y. S. Jung, *Advanced Energy Materials*, 1800035 (2018).
- “Flexible, Solid-State Lithium Ion-conducting Membrane with 3D Garnet Nanofiber Networks,” K. Fu, Y. Gong, J. Dai, A. Gong, X. Han, Y. Yao, Y. Wang, C. Wang, Y. Chen, C. Yan, E.D. Wachsman, and L. Hu, *Proceedings of the National Academy of Sciences*, **113**, 7094-7099 (2016)